

CATALYTIC HYDROTREATMENT OF COAL-DERIVED NAPHTHA

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ABSTRACT

A naphtha derived from the liquefaction of a subbituminous (Black Thunder) and a bituminous coal (Ill. #6) was hydrotreated on a pilot plant scale, to provide a feedstock sufficiently low in heteroatoms for further studies in reforming. Two commercial catalysts, a Ni/Mo and Co/Mo on alumina, were employed in the processing of the naphtha samples. The Black Thunder naphtha was processed for over 120 hours for two passes using a Co/Mo catalyst and once using a Ni/Mo catalyst. For this naphtha, the nitrogen removal was extremely difficult using the catalysts and conditions employed in this study. An average of 51.6% of the nitrogen was removed for the three passes. The oxygen compounds in this naphtha were relatively easily removed. During the first pass over the Co/Mo catalyst, 94.0% of the oxygen was removed. Further processing during the next two passes using a Co/Mo and a Ni/Mo catalyst further reduced the oxygen content by 54% and 40% respectively.

INTRODUCTION

The dominance of gasoline as a transportation fuel in the United States dictate that any viable coal liquefaction technology must produce a naphtha feedstock that can be upgraded for gasoline production. The concept of what a "good" gasoline is has changed over the decades depending on availability of crudes, environmental concerns, etc. One of the major problems associated with a naphtha derived from processing coal is the high heteroatom content. In order to reform a coal-derived naphtha, the heteroatom content must be further reduced by hydrotreating.

HDN and HDO has been studied extensively using model compounds to determine the mechanism (1-3) and for evaluation of catalysts (4). However, few studies have addressed the upgrading of coal-derived naphtha on a pilot plant scale (5). In the present study, the hydrotreatment of a subbituminous coal-derived naphtha was catalytically hydrotreated in the CAER pilot plant. Two commercial hydrotreating catalysts (Ni/Mo and Co/Mo on alumina) were employed in this study.

EXPERIMENTAL

Naphtha Feedstock

Three, 55 gallon drums of the naphtha were obtained from the Wilsonville, Alabama Advanced Integrated Two Stage Liquefaction pilot plant. The naphtha hydrotreated was obtained from processing a Black Thunder coal (subbituminous).

Pilot Plant Operations

The naphtha was hydrotreated in the reconfigured CAER 1/8 tpd liquefaction pilot plant. The process diagram is shown in Figure 1. The plant consists of the following sections: (a) feed delivery (naphtha, H_2), (b) reactor, and (c) high and low pressure separators. The reactor was charged with 2 kg of catalyst and operated in a fixed bed down-flow configuration for the hydrotreating operations.

The first catalyst employed was a commercial Co/Mo on alumina catalyst (American Cyanamid HDS-1442A, 1/16" x 1/4" pellets). The second catalyst studied was a commercial Ni/Mo on alumina catalyst (Akzo KF-840 1.3Q).

Both catalysts were presulfided using a mixture of 3% H_2S in hydrogen prior to the beginning of hydrotreating operations. During the presulfiding operation, a flowrate 30 $ft.^3/h$ of the H_2S/H_2 mixture was used. The reactor temperature was rapidly increased to 175°C followed by a 25°C/h ramp. During these operations, the composition of the gas stream exiting the plant was continuously monitored for the H_2S breakthrough by an on-line gas chromatograph. During the ramping of the reactor temperature, the data obtained from the GC indicated that no additional H_2S was being absorbed by the catalyst. At this point, the temperature was increased to 375°C and held at this temperature for 90 minutes. The reactor temperature was then cooled to 300°C and the inlet gas stream was switched to hydrogen using a flowrate 5 $ft.^3/h$ prior to the start of naphtha processing. The same presulfiding procedure was used for operations with the Ni/Mo catalyst.

The processing conditions for the three pilot runs are given in Table 1. During naphtha processing, daily samples from the low pressure separator (V-451) were obtained for analysis. The pilot plant was placed under nitrogen at a system pressure of 360 psig prior to the beginning of the second hydrotreating run. Prior to the third pilot plant run, the Co/Mo catalyst was replaced by the Ni/Mo catalyst.

During the hydrotreating operations, two barrels of the Black Thunder naphtha was processed. Collection of the hydrotreated naphtha from each pass into the product barrel was initiated upon the attainment of steady state conditions as indicated by the process variables and the nitrogen content of the daily samples. The feedstock for the second pass using the Black Thunder naphtha was the product barrels obtained during the first pass. The feedstock for the third pass using the Ni/Mo catalyst was the hydrotreated product from the second pass.

Oxygen analyses were performed using the FNA method and were provided by the University of Kentucky Radioanalytical Services. Trace level nitrogen was analyzed using a Xertex DN-10 total nitrogen analyzer equipped with a chemiluminescence detector.

RESULTS AND DISCUSSION

Black Thunder Hydrotreatment

The nitrogen content of the hydrotreated naphtha (daily samples) obtained during the three passes are shown in Figure 2. The data clearly show the difficulty in removing the nitrogen from the naphtha using either the Co/Mo or Ni/Mo catalysts using these process conditions. During the initial pass, only 43% of the nitrogen was removed from the naphtha. The amount of nitrogen during the second pass was only marginally better (51%). Switching to a Ni/Mo catalyst and using the same process conditions did increase the nitrogen removal to 61%. However, after three passes, the nitrogen content of the hydrotreated naphtha remained at an average level of 383 ppm. The average nitrogen removal was only 52% for all three passes. Based on these data, it was projected that to obtain a hydrotreated product containing 2 ppm nitrogen, the naphtha would have to be processed 10 times (Figure 3). Clearly, hydrotreatment of the Black Thunder naphtha will require more severe conditions than are normally employed in petroleum refining to obtain a final product in which the nitrogen content is sufficiently low for further upgrading by reforming.

The amount of oxygen in the hydrotreated Black Thunder naphtha is shown in Figure 4. Although the oxygen content of the original naphtha is high (2.01%), 94% of the oxygen was removed during the first pass to yield a product containing .11% oxygen. The second and third pass (Ni/Mo) removed an additional 54% and 40% of the oxygen to produce a final hydrotreated naphtha containing .03% oxygen. The results indicate that the majority of the oxygen was easily removed during the first pass using the Co/Mo catalyst and low oxygen content of naphtha feedstock not substantially improve the amount of nitrogen removed during the second pass.

It is apparent from these data, that oxygen is easily removed from the Black Thunder (subbituminous coal) naphtha. The nitrogen compounds found in this naphtha are more difficult to remove during hydrotreating using a WHSV of 1 and a reaction temperature of 403°C. The data also suggests that the HDN process did not substantially inhibit the HDO process using either the Co/Mo or Ni/Mo catalysts under these conditions.

CONCLUSIONS

The resulting data from the hydrotreatment of a Black Thunder naphtha indicate that the removal of nitrogen is difficult. To obtain a nitrogen content of less than 10 ppm require process conditions which are more severe than normally associated with petroleum hydrotreating. In contrast to the difficulty in obtaining a low nitrogen product, oxygen is relatively easy to remove from the Black Thunder naphtha. It is apparent from these data that new catalysts will have to be developed for the processing of coal-derived

naphtha to obtain a sufficiently heteroatom free product using common industrial process conditions.

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TABLE 1

Process Summary

Black Thunder Hydrotreatment

<u>Pass #</u> <u>(Run Hours)</u>	<u>Catalyst</u>	<u>Feed Rate</u> <u>(#/hr)</u>	<u>WHSV</u> <u># feed/# catalyst/hr</u>	<u>Temp</u> <u>(°C)</u>	<u>Pressure</u> <u>(psig)</u>
1 (0-165)	CoMo	4.0, 4.5	.9, 1.0	418	2010
2 (0-143)	CoMo	4.0, 4.5	.9, 1.0	418	2010
3 (0-127)	NiMo	4.5	.8	403	2000

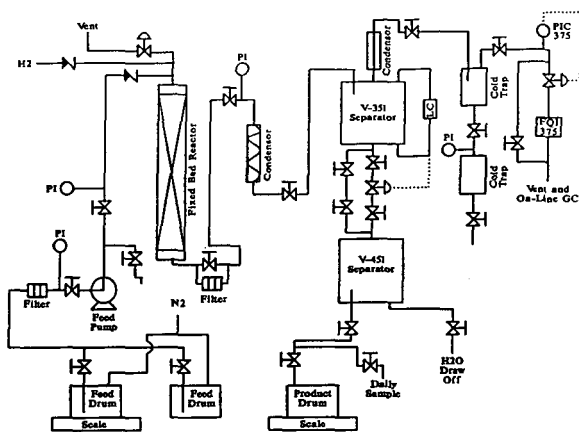


Figure 1. CAER Pilot Plant configuration for naphtha hydrotreating.

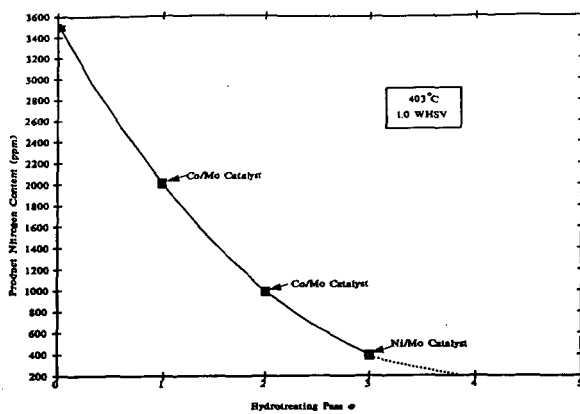


Figure 2. Summary of HDN for Black Thunder hydrotreatment.

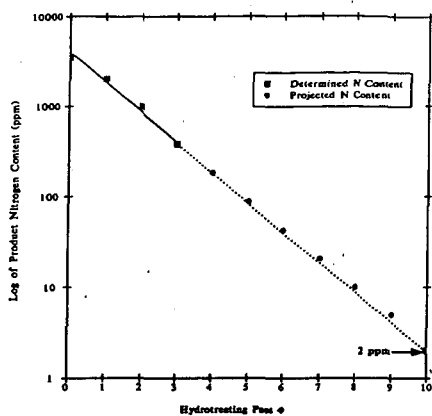


Figure 3. The projected number of passes to obtain a Black Thunder product containing 2 ppm nitrogen.

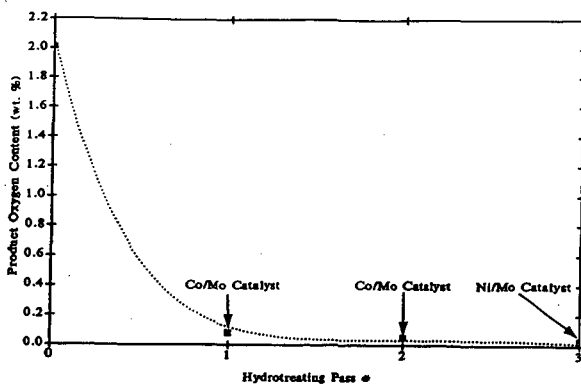


Figure 4. Summary of HDO for Black Thunder hydrotreatment.